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ELECTRODE PROCESSES

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Anodic Platinum Losses in Chlorate Electrolytes

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ANODIC PLATINUM LOSSES IN CHLORATE ELECTROLYTES

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ABSTRACT

Radioactive platinum 197 was used as a tracer in the examination
of factors influencing anodic platinum losses in aqueous chlorate and per-
chlorate electrolytic solutions. Losses were greatest in the presence of
chlorides and were probably attributable to the formation of soluble oxy-
chlorides by reaction of chloride ions with platinum(IV) oxide or platinum(VI)
oxide at the electrode surface. Losses were negligibly small in chlorate
solutions in the absence of chloride ions.

INTRODUCTION

Although much time and effort has been devoted to establishing the ideal conditions for the anodic oxidation of chlorate to perchlorate, little has been published about anodic platinum losses in such cells. On a laboratory scale this loss of platinum is insignificant; however, in the industrial operation of perchlorate cells it is a subject of great concern.

Very little data has appeared in the literature concerning the influence of the various factors on anodic platinum loss except that observed in industrially operated perchlorate cells. Among the few laboratory results are those of Schumacher[1], who reported that with a laboratory cell set up to determine the influence of temperature, current density and pH on anodic loss of platinum, the platinum loss increased with increasing temperature in the range 40 degrees C. to 65 degrees C. and with increasing current density in the range 2 to 3 amperes per square inch. Observations on industrially operated perchlorate cells support Schumacher's findings with the added indication that platinum loss is highest at low pH[2]. Unfortunately, such factors as high current density and low pH which favor high platinum loss also favor high current efficiency for perchlorate production so that it is usually necessary to compromise; the goal being the highest current efficiency with lowest platinum loss. Platinum losses range from 3 mg. to about 12 mg. per kilogram of perchlorate formed.

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[1] J. C. Schumacher, Trans. Electrochem. Soc., 92, 45 (1947).

[2] Pennsylvania Salt Mfg. Company, Technical Report to the Office of Naval Research, Chemistry Branch (Contract No. Nonr-372(00)) August 31, 1951.

The work reported in the following sections was undertaken in order to determine more specifically the reasons for anodic platinum losses in perchlorate cells. Radioactive tracers were used in order to detect extremely small amounts of platinum, thus permitting a more detailed analysis of trends.

APPARATUS, MATERIALS, AND METHODS

Electrolytic Cells.

Electrolysis was carried out in 400 ml. pyrex beakers, and in the experiments requiring a diaphragm cell, an unglazed porcelain cup of 52 mm. diameter and 100 mm. height was inserted into the beaker to serve as the anode compartment.

In cells without a diaphragm, the electrolyte was stirred with an air stirrer provided with a stainless steel propeller coated with "Ucilon".* In the diaphragm cell, just the anolyte was agitated with a smaller glass propeller. Anodes were fabricated from 0.002 inch thick pure platinum sheets and were 1 cm. x 1 cm. Each anode was provided with a small tab to which a wire lead was connected by folding the tab over the wire then pressing the tab securely against the wire in order to assure electrical contact and good mechanical support. A one-half inch long, No. 16, platinum wire, sealed in Pyrex glass and supported by a glass bridge, served as the lead to the anode. The sealed in end of the platinum wire was soldered to a six inch long copper wire.

Radiochemical Measurements.

The quantitative determination of platinum was done by measurement of the activity of radioactive platinum 197. The electrodes and a small piece of platinum sheet of known weight were thoroughly cleaned with hot concentrated nitric acid and then irradiated in the X-10 reactor at Oak Ridge for 24 hours. From the known weight of the platinum the specific activity was determined and used in subsequent measurements for determination of platinum. Together with the 18-hour platinum 197 there is also

*United Chromium, Inc., protective coating material.

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formed in the reactor the 31-minute platinum 199, which decays to 3.3-day gold 199[3] giving rise to the problem of distinguishing between the platinum and gold activities. This was accomplished by counting the samples as soon as possible and counting again at a later time, when the platinum 197 activity was negligible. This activity attributable to gold 199 was extrapolated to the time of the first count and subtracted from it, the difference being the platinum activity. In the later experiments a Tracerlab dipping counter tube type TGC-5 was used. Activities determined in solution with that tube were found to be essentially those of the higher energy beta particle of platinum 197.

In earlier experiments, the activity was determined by placing a small volume of the liquid sample in weighing capsules and counting with a Tracerlab TGC-2 mica end-window counter tube. Platinum cathodes were counted on both sides using the same apparatus with the exception that planchets were used in place of the weighing capsules.

In later experiments, comprising the majority of those reported, the dipping counter was used in counting solutions without further preparation. Although the dipping tube was thoroughly washed with distilled water after each count, the background activity, obtained by counting inactive 5 $\underline{N}$ sodium chlorate solution, varied sufficiently to warrant an individual background count previous to each sample count.

In general the activity of the samples in the weighing capsules reached about 200 counts per minute as a maximum. With the dipping counter tube, the activity ranged from 100 to 5000 counts per minute.

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[3] United States Department of Commerce, National Bureau of Standards Circular No. 499, September 1, 1950.

Chloride Analysis.

The chloride ion concentrations were approximated turbidimetrically as silver chloride, using an Evelyn photoelectric colorimeter with a blue filter. For this measurement, 5 ml. of the sample was added, with stirring, to 25 ml. of 0.02 N silver nitrate solution and allowed to stand for 5 minutes before measurement.

Coprecipitation Experiments.

In an attempt to determine the platinum species in solution due to the anodic dissolution, coprecipitation experiments were carried out by adding slightly soluble inactive potassium hexachloroplatinate(IV) or platinum(IV) oxide 4-hydrate to fifty milliliters of the active anolyte. The suspension was vigorously agitated for a specified length of time in a test tube 40 mm. in diameter and 20 cm. high.

The suspension was then centrifuged, the supernatant solution diluted with water, and the activity determined with a dipping tube. The precipitate was dissolved and counted in a like manner. Potassium hexachloroplatinate(IV) was dissolved in a relatively larger amount of water while the hydrated platinum oxide was dissolved in dilute potassium hydroxide. The quantity of the platinum(IV) oxide 4-hydrate and potassium hexachloroplatinate(IV) in the filtrate and precipitate was determined as potassium hexachloroplatinate(IV) which is insoluble in concentrated aqueous potassium chloride.

Experiments were also carried out with hydrated aluminum oxide in which suspensions were treated similarly to those of the platinum compounds. However, the centrifuged oxide was suspended in 1 N sodium hydroxide and the activity of the solid phase determined in the suspension.

Potassium hexachloroplatinate(IV).

The potassium hexachloroplatinate(IV) was prepared in the usual manner by dissolving platinum sheet in aqua regia, evaporating twice with hydrochloric acid, and precipitating with concentrated aqueous potassium chloride.

Platinum(IV) oxide 4-hydrate.

For the preparation of platinum(IV) oxide 4-hydrate, a modification of the method described by Bellucci[4] was used. Sixty milliliters of 15 $\underline{M}$ aqueous sodium hydroxide was added slowly, with stirring, to a solution containing 25 ml. of Fisher, 10 percent platinum(IV) chloride solution diluted with an equal volume of water. The solution was allowed to boil gently on a hot plate for a half hour, during which time the volume was kept approximately constant by the occasional addition of water. On boiling the orange color of hexachloroplatinate(IV) changed to the light yellow sodium platinate(IV). The sodium platinate(IV) solution was then cooled to room temperature and added slowly and with stirring to an ice cold solution of 70 ml. glacial acetic acid in 500 ml. water, to which a little cracked ice had been added. At this time the pale yellow platinum oxide precipitated. Stirring was continued for an hour, after which time the precipitate was separated by centrifugation and washed twice with 100 ml. portions of water. The precipitate was dissolved in a small volume of 0.1 N potassium hydroxide, filtered, and reprecipitated by adding 0.1 N perchloric acid dropwise, with vigorous stirring. The platinum(IV) oxide 4-hydrate was filtered on sintered glass, washed with one 10 ml. portion

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[4]Bellucci, Z. Anorg. Chem. 44, 168 (1905).

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of water**, and dried in air at room temperature. <u>Anal.</u> Calcd.: Pt, 65.23; 0 (excluding H_2O), 10.69. Found: Pt, 64.96, 65.23; 0, 10.47, 10.54.

**The hydrated oxide tends to peptize, thus permitting only one washing.

Electrolytic Measurements.

The first experiments were carried out in cells in which no attempt was made to separate anode and cathode solutions. Because of the many difficulty resolvable variables, only qualitative observations were made. In those experiments the electrolyte comprised 200 ml. of solution in which the total concentration of $NaClO_3$ and $NaClO_4$ was 5.3 $\underline{M}$. Anodic platinum loss was determined in each case after electrolysis for 8 hours at a current of 0.8 amperes.

Total platinum loss (active platinum in solution plus that plated at the cathode) appeared to increase markedly at higher mole fractions of perchlorate. The loss was especially high in the $NaClO_4$ electrolyte. Under otherwise identical conditions the losses at 40 degrees C. were con_ siderably higher than those at 30 degrees C. (about 50 times for the $NaClO_3$ electrolyte but only 6 times for the $NaClO_4$ electrolyte), and increased slowly from 0 to 1 mole fraction of $NaClO_4$ (moles $NaClO_4$/moles $NaClO_4 +$ moles $NaClO_3$). The platinum plated on the cathode represented about 1/10 of the total loss for chlorate cells, and about 1/5 for the cells contain_ ing perchlorate solutions only.

In addition to chlorate and perchlorate, the anion most frequently found in solutions of the type under consideration is chloride. In order to determine the relative effect of the presence of chloride in electrolyte solutions, an experiment was done in which 10^{-2} moles per liter of $NaCl$ was added to 5.3 $\underline{M}$ $NaClO_4$ solution and electrolysis was carried out at 40 degrees C. under the same conditions as those mentioned previously. The total platinum loss was twice that of the $NaClO_4$ with no chloride added,

However, only a trace of platinum plated on the cathode. In the course of electrolysis the pH rose from 5 to 8 and the chloride concentration fell to ca 5 X 10^{-3} M.

In order to determine further the effect of chloride on platinum loss, amounts of NaCl ranging from 3 X 10^{-4} to 1 X 10^{-2} moles per liter were added to 5.3 M NaClO$_3$ solution, which was 10^{-2} M in HClO$_3$, and electrolysis was carried out for a period of 8 hours at 0.55 amperes and at 40 degrees C. In the course of the experiment the pH rose to a value which increased with increasing initial chloride concentration. At the same time the chloride ion concentration decreased and the platinum loss increased. At low chloride ion concentration the rate of loss increased with increasing chloride ion concentration, but at the higher concentrations the rate decreased. It was felt that the decrease in the last experiments was largely attributable to increase in pH due to chloride ion discharge during electrolysis. It is well known that platinum losses may be minimized by increase in pH, although at the expense of perchlorate yield.

Prolonged electrolysis of 5.3 M NaClO$_4$ solution, in the absence of chlorate and chloride, resulted in the formation of a brown film on the anode surface. In experiments in which small amounts of chloride were added the film failed to appear until the chloride concentration was negligibly small. The film was amorphous so that attempts to characterize the substance by X-ray methods were unsuccessful. The substance was insoluble in 3 M chloric acid, 5.3 M sodium chlorate, and concentrated nitric acid, but was readily soluble in both dilute and concentrated hydrochloric acid. A hydrochloric acid solution of the material was shown to contain platinum by addition of tin(II) chloride and extraction of the tin(II)-platinum complex into ethyl acetate.

Although the film did not dissolve in 5.3 M sodium chlorate solution electrolysis of such a solution using the coated platinum as anode resulted in rapid dissolution of the material.

In order to maintain an acid solution at the anode, in subsequent experiments cells were used in which the anolyte was placed in a porous cup set into a larger vessel which contained the catholyte. The anolyte comprised 100 ml. of electrolyte solution and the catholyte, 150 ml. of solution which was frequently, although not always, initially the same as that used as the anolyte. Platinum losses were calculated on the basis of total platinum in both anolyte and catholyte solutions.

Platinum loss as a function of time is shown in Figure 1 for a series of experiments in which the anolyte was composed of 5.2 moles per liter sodium chlorate, 0.01 moles per liter sodium chloride, and 0.03 moles per liter chloric acid. In each case the catholyte was 5.2 $\underline{M}$ sodium chlorate. Electrolysis was carried out at 0.5 amperes and at 30 degrees C. The corresponding change in chloride ion concentration may be seen from the data of Table 1, which were derived from the same experiments. In two experiments additional chloride was added after 7 hours of electrolysis, at which time the initial chloride had been reduced to approximately 0.3% of its original concentration. In those two cases an additional platinum loss was observed, which appeared to be essentially a function of the concentration of chloride added.

In order to minimize the effect of chlorides on the anodic platinum loss, solutions of sodium chlorate and sodium perchlorate, each of which was made 0.03 $\underline{M}$ in the parent acid, were electrolyzed for 10 hours at 0.1 ampere prior to their use in radiochemical experiments. Results of experiments in which those solutions were used in the preparation of the electrolyte solutions are given in Table 2. The comparable loss, for a solution of sodium chlorate (0.03 $\underline{M}$ chloric acid) which had not been pre-electrolyzed was 161 micrograms for 7 hours electrolysis.

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Figure 1. Variation of platinum loss with time of electrolysis.

Conditions: 0.5 amperes, 30 degrees C. Anolyte: 5.2 $\underline{M}$

$NaClO_3$, 0.03 $\underline{M}$ $HClO_3$, 0.01 $\underline{M}$ NaCl. Catholyte: (initial)

5.2 $\underline{M}$ $NaClO_3$. (a) 0.005 moles per liter NaCl added after

7 hours (b) 0.01 moles per liter NaCl added after 7 hours.

PLATINUM LOSS (MICROGRAMS)

TIME IN HOURS
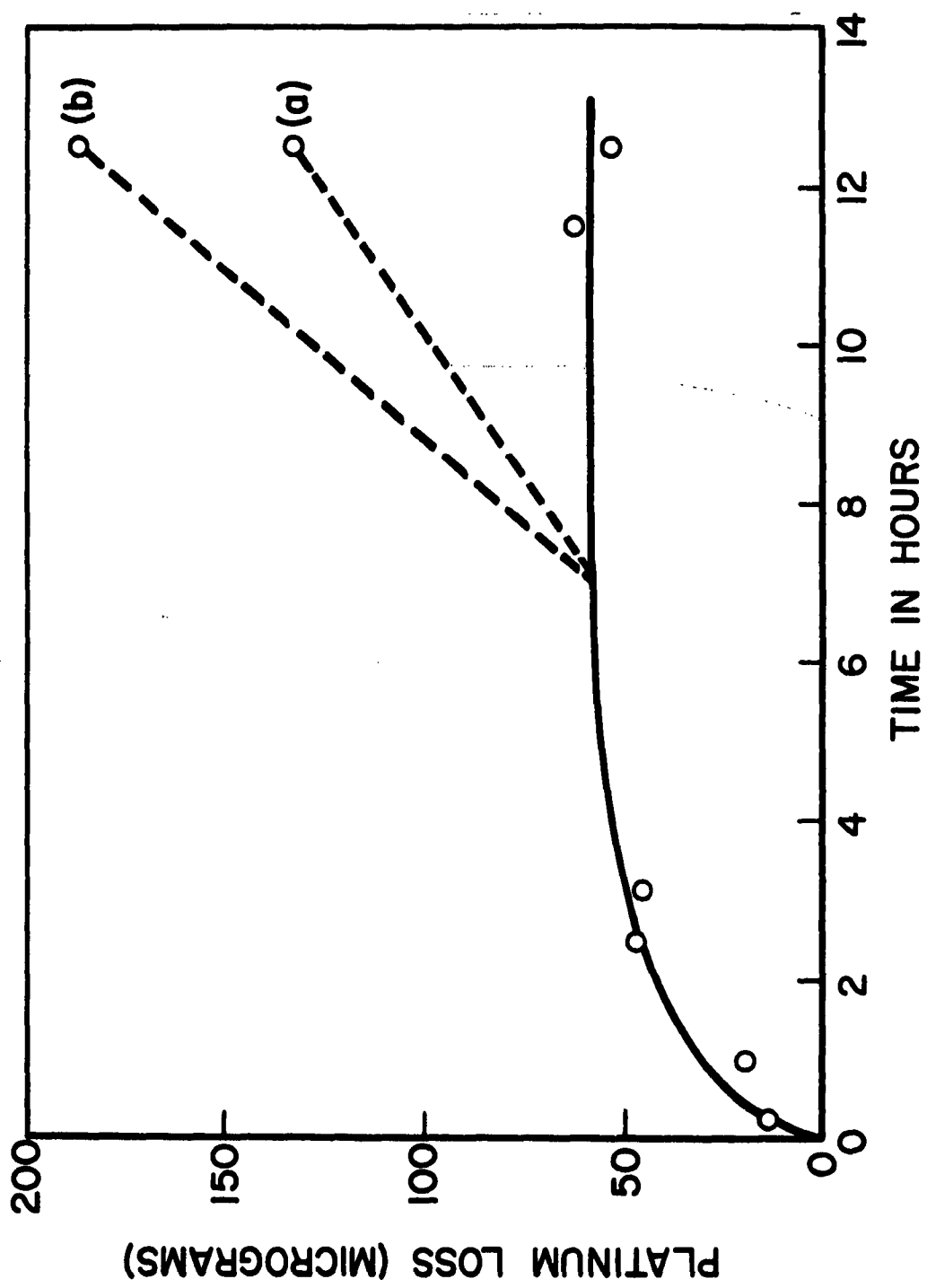
Figure 1

Time of Electrolysis (hours)	Chloride ion concentration (final) (moles per liter)
0.25	3.5×10^{-3}
1.00	2.5×10^{-3}
3.25	2.0×10^{-3}
7.00	1.0×10^{-5}
11.50	1.0×10^{-6}
12.50	5.0×10^{-7}

TABLE 2

Pre-electrolyzed solutions.

Anodic platinum loss as a function of solution composition; 0.5 amperes, 30 degrees C., 7-hour electrolysis.

$NaClO_3$ (moles per liter)	$NaClO_4$ (moles per liter)	Platinum loss micrograms
5.2	-	8
4.2	1.0	7
1.0	4.2	21
-	5.2	174

Chloride is a common impurity in sodium chlorate. Although reagent grade chemicals were used, the concentration of chloride ion in aqueous 5.2 $\underline{M}$ sodium chlorate was as high as 2×10^{-4} $\underline{M}$. The chloride ion concentration, however, was negligible in a sodium perchlorate solution of the same concentration. As a comparison with experiments using pre-electrolysed solutions and to find the platinum loss as a function of acidity, electrolysis experiments were carried out using 5.2 $\underline{M}$ NaClO$_3$ and 5.2 $\underline{M}$ NaClO$_4$ solutions at different acidities, the other conditions being the same as in previous experiments. The results of these experiments are shown in Table 3. In cells containing perchlorate solutions only, no appreciable difference in platinum loss was observed between pre-electrolysed and non-pre-electrolysed material, however, the non-pre-electrolysed chlorate anolyte gave a considerably higher loss than the pre-electrolysed chlorate solution.

Platinum losses using 5.0 $\underline{M}$ sodium nitrate solutions, acidified with nitric acid, as anolyte were slightly less than the losses in sodium perchlorate cells of corresponding acidity.

It was apparent from the preceding experiments that the presence of chloride ion in the anolyte was an important factor contributing to platinum loss. Pre-electrolysis of the experimental solutions resulted in a decrease in the platinum loss, thus substantiating that conclusion. An effective method of reducing chloride ion concentration in aqueous solution is by precipitation with silver ion. Accordingly, two experiments were carried out in which electrolyte solutions were treated with AgClO$_4$ and the AgCl precipitate was removed by centrifugation. The supernatent solution was essentially free of chloride ion, but contained silver and perchlorate ions.

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TABLE 3

Solutions non-pre-electrolysed.

Anodic platinum loss as a function of initial acidity. Anolyte:
5.2 $\underline{M}$ NaClO$_3$ or 5.2 $\underline{M}$ NaClO$_4$. 0.5 amperes, 30 degrees C. 7-hour electrolysis.

		Platinum loss (micrograms)
NaClO$_x$ solutions:	1 $\underline{M}$ NaOH	57
(Catholyte-5.2 $\underline{M}$	Neutral	125
NaClO$_3$ only)	0.03 $\underline{M}$ HClO$_3$	161
	0.10 $\underline{M}$ HClO$_3$	483
NaClO$_3$ solutions	0.10 $\underline{M}$ HClO$_3$	374
(Catholyte-5.0 $\underline{M}$		
NaNO$_3$ only)		
NaClO$_4$ solutions	0.03 $\underline{M}$ HClO$_4$	182
(Catholyte-5.2 $\underline{M}$	0.10 $\underline{M}$ HClO$_4$	549
NaClO$_4$		

Results of experiments in which the pre-treated electrolyte was used are given in Table 4. The acidities at which those experiments were carried out were typical of those for which high platinum losses were observed in earlier experiments.

TABLE 4

Solution pre-treated with $AgClO_4$: Anodic platinum loss as a func- of acidity; 5.2 $\underline{M}$ $NaClO_3$, 0.005 $\underline{M}$ $AgClO_4$, 0.5 amperes, 30 degrees C., 7-hour electrolysis.

$HClO_3$ (moles/liter)	Platinum loss (micrograms)
0.03	0.5
0.10	4.0

Coprecipitation Experiments.

From evidence in preceding experiments the marked influence of chloride ion concentration on anodic platinum loss was apparent. In an attempt to obtain a better insight as to the platinum species in solution due to anodic dissolution of platinum in chlorate electrolytes, coprecipitation experiments were undertaken with potassium hexachloroplatinate(IV), in which the anion is fully chlorinated, and platinum(IV) oxide 4-hydrate. The experiments were carried out by adding the inactive platinum compound to 50 ml. of the anolyte solution which had been previously electrolyzed for 7 hours, at 30 degrees C., and at a current of 0.5 amperes, the initial anolyte composition being 5.2 $\underline{M}$ $NaClO_3$, and 0.1 $\underline{M}$ $HClO_3$. Under the same conditions adsorption studies of the unknown platinum species on aluminum

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oxide hydrate ($Al_2O_3 \cdot H_2O$) were also made.

The results of these experiments are shown in Table 5.

TABLE 5

Coprecipitation experiments made with the unknown platinum species
in solution after the electrolysis: Anolyte 5.2 $\underline{M}$ $NaClO_3$, 0.1 $\underline{M}$ $HClO_3$. 0.5 amperes
30 degrees C., 7-hour electrolysis.

Compound added	Amount added (grams)	Reaction time (hours)	Distribution of carrier (solid/solution)	Distribution of activity (solid/solution)
K_2PtCl_6	2.4375	4.5	1.23	0.034
$PtO_2 \cdot 4H_2O$	0.500	0.3	0.51	0.34
	0.500	4.0	0.32	0.52
	1.2847	4.5	1.09	0.40
	0.500	16.5	0.074	0.71
$Al_2O_3 \cdot H_2O$	1.00	16.0	0.77	0.058

Based on the results of the distribution of activity between the
carrier and the unknown platinum species in solution after electrolysis,
it is probable that the dominant species more closely resembles the oxide
than it does the hexachloroplatinate(IV).

In order to determine the stability of hexachloroplatinate(IV) ions
in typical electrolyte solutions, coprecipitation experiments were done
using potassium hexachloroplatinate(IV) as a carrier for radioactive hexa-
chloroplatinic acid in chloride and chlorate media. The concentration of
the radioactive hexachloroplatinic acid was of the same order of magnitude

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as the concentration of the platinum species in solution due to the anodic
platinum dissolution in chlorate electrolysis under the same conditions
as those used in previous experiments. For comparison, a coprecipitation
experiment was done with K_2PtCl_6 carrier and radioactive H_2PtCl_6 in aqueous
2 $\underline{M}$ KCl in which hexachloroplatinate(IV) ion is stable with respect to hy-
drolysis. The results of those experiments are listed in Table 6.

TABLE 6

Volume of solution: 50 ml. Amount of K_2PtCl_6 carrier added: 1
gram. Radioactive H_2PtCl_6 concentration: 1.3 x 10^{-5} $\underline{M}$. (A) Medium:
Aqueous 2 $\underline{M}$ KCl. Reaction time: 4 hours. Carrier added immediately
following the addition of the radioactive hexachloroplatinic acid. (B)
Medium: aqueous 5.2 $\underline{M}$ $NaClO_3$, 0.1 $\underline{M}$ $HClO_3$. Reaction time: 4 hours.
Carrier added immediately following the addition of the radioactive hexa-
chloroplatinic acid. (C) Medium: aqueous 5.2 $\underline{M}$ $NaClO_3$, 0.1 $\underline{M}$ $HClO_3$.
Reaction time: 12 hours. Carrier added 4 hours after the addition of
the radioactive hexachloroplatinic acid.

Experiment	Distribution of carrier solid/solution	Distribution of activity solid/ solution
A	6.20	0.36
B	0.59	0.058
C	0.52	0.001

DISCUSSION

Radiochemical experiments were limited in scope because of the short half-life (18 hrs.) of radioactive platinum 197. Nevertheless, it is felt that the results of these experiments give some insight into the factors influencing platinum losses in chlorate-perchlorate cells.

With chlorate electrolytes in which the chloride ion concentration was negligibly low, platinum losses were extremely small. In the presence of even small chloride concentrations, such as those present as impurities in a typical solution of reagent grade sodium chlorate (in 5.2 $\underline{M}$ NaClO$_3$ the chloride concentration was 2×10^{-4} $\underline{M}$), the losses were significantly large. Addition of sodium chloride in excess of that normally present as contamination resulted in increased dissolution of platinum, and the addition of increments of chloride after electrolysis had proceeded long enough to rid the solution of their original chloride ion contents resulted in additional platinum losses very nearly proportional to the amounts of chloride added. There seems to be little reason to doubt that the principal cause of platinum dissolution in chlorate electrolytes was the presence of chloride ions, either as original contamination or as the product of cathodic reduction of chloride containing species. In diaphragm cells, the electrolysis of chlorate solutions in which the chloride was removed by precipitation with silver ion or by pre-electrolysis, resulted in the expected decrease in anodic platinum loss. Among other factors causing increased platinum loss was an increase in acidity.

Electrolytic oxidation of chlorate to perchlorate at the platinum anode has been attributed to the formation of an unstable higher oxide of

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platinum (presumably PtO_3) at the electrode surface. Early observers[5] proposed the formation of an anode film of PtO_3 which was obtained at high current densities. It is doubtful that gross amounts of the highly oxidised material were obtained in the light of later results. Experiments were reported in the literature[6] in which practically pure $PtO_2.nH_2O$ was deposited in the anode compartment after electrolysis of dilute sulfuric aicd at a platinum anode. The nature of the oxide was determined by ordinary analytical methods. In these experiments an "undulant" current (an alternating current superimposed on direct current) was used. On the basis of this report it is supposed that the film observed at the platinum anode after the electrolysis of concentrated aqueous sodium perchlorate was a hydrated platinum(IV) oxide. Whether the film is comprised of $PtO_2.nH_2O$ or PtO_3 it may be presumed that the dissolution of the oxide in dilute hydrochloric acid led to the formation of soluble oxychlorides, and is the principal contributer to anodic platinum losses accompanying the electrolysis of aqueous chlorates.

Although coprecipitation experiments yielded only suggestive results, they showed quite clearly that hexachloroplatinate(IV) ions were unstable under the electrolytic cell conditions employed. Because of the greater percentage coprecipitation of the product of anodic dissolution with platinum(IV) oxide 4-hydrate it may be argued that the solution species of principal concern are oxycations or oxychlorides, probably having a wide range of compositions.

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[5] J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. 16, Longmans, Green and Co., New York, (1937) p. 245.

[6] S. Altmann and R. H. Busch, Trans. Faraday Soc. 45, 720 (1949).

Although the presence of chloride substantially increased the anodic platinum losses resulting from the electrolysis of perchlorate solutions, platinum losses were significant in essentially chloride free perchlorate electrolytes. This phenomenon may be attributed to the higher anode potential exhibited in such solutions.[7] Substitution of nitrate ions for perchlorate ions led to relatively little change except to decrease platinum dissolution slightly.

The importance of stable chloride-containing platinum solution species to the complete understanding of anodic platinum loss receives substantiation from comparison of detailed results obtained in experiments with perchlorate electrolytes in the presence and absence of chloride ions. Under otherwise comparable conditions the larger solution concentrations of platinum species were observed in the presence of chloride while the greater cathode deposits of platinum were observed in its absence. It must be concluded that the presence of chloride was responsible for the formation of a more stable solution species.

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[7]J. W. Hackett and M. A. Fineman, Dept. of Chemistry, Providence College, Technical Report to the Office of Naval Research, Contract Nonr-1213(00), December 31, 1953.

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